Photophysical properties of porphyrin–single-walled carbon nanotube linked systems with various spacer lengths

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Although the precise understanding of the intrinsic nature of the exciplex state with both excited state and charge-transfer characters is crucial for efficient formation of the long-lived charge-separated state, the information is extremely limited in comparison with the charge-separated state because of lack of suitable model systems and difficulty in creating such model systems.

We report herein unprecedented long-range observation of both formation and decay of the exciplex state in donor (D)–bridge (B)–acceptor (A) linked systems. Zinc-porphyrins (ZnP) as a donor were tethered to single-walled carbon nanotube (SWNT) as an acceptor through oligo(*p*-phenylene)s (ZnP-ph$_n$-SWNT) or oligo(*p*-xylene)s (ZnP-xy$_{n-1}$-ph$_1$-SWNT) with systematically varied lengths (n = 1–5) to address the issue (Figure 1). Exponential dependencies of rate constants for the exciplex formation (k_{FEX}) and decay (k_{DEX}) on the edge-to-edge separation distance between ZnP and SWNT through the bridges were unambiguously derived from time-resolved spectroscopies. Distance dependencies (i.e., attenuation factor, β) of k_{FEX} and k_{DEX} in ZnP-ph$_n$-SWNT were found to be considerably small (β = 0.10 for k_{FEX} and 0.12 Å^{-1} for k_{DEX}) compared to those for charge separation and recombination (0.2−0.8 Å^{-1}) in D–B–A systems with the same oligo(*p*-phenylene) bridges. The small β values may be associated with the exciplex state with mixed characters of charge-transfer and excited-states. In parallel, the substantially non-conjugated bridge of oligo(*p*-xylene)s exhibited larger attenuation values (β = 0.12 for k_{FEX} and 0.14 Å^{-1} for k_{DEX}). These results provide deep insight into the unique photodynamics of electronically strongly coupled D–B–A systems involving exciplex.

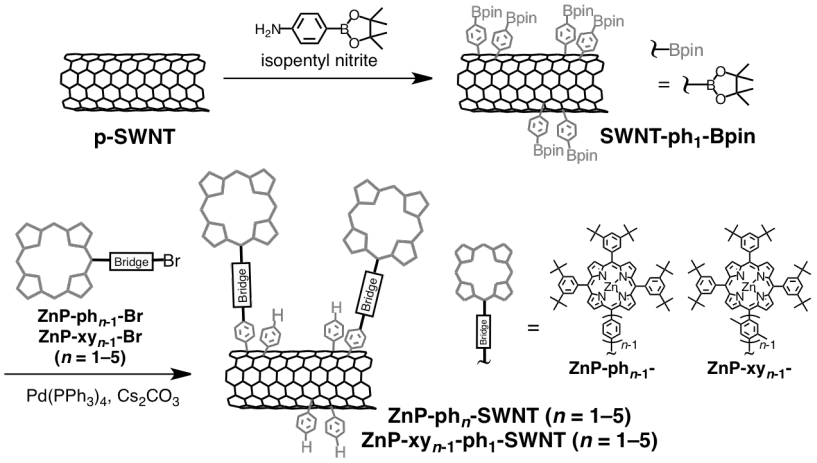

Figure 1. Synthesis of ZnP-ph$_n$-SWNT and ZnP-xy$_{n-1}$-ph$_1$-SWNT (n = 1 – 5).

[1] J. Baek, T. Umeyama, K. Stranius, H. Yamada, N. V. Tkachenko, and H. Imahori, *J. Phys. Chem. C*, **121**, 13952-13961 (2017).